Final Report DE-FG36-01ID14008

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Written by: John R. Dorgan

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Project Contact(s): **Technical:** John Dorgan, 3032733539, jdorgan@mines.edu
Business: Mary Mittag-Miller, 3032733405, mmittag@mines.edu

DOE Project Team:

DOE-HQ contact – Valerie Sarisky-Reed, 202-586-8014, Valerie.Sarisky-Reed@ee.doe.gov
DOE Field Project Officer – Fred Gerdeman, 303 275-4928, fred.gerdeman@go.doe.gov
DOE Contract Specialist – Margo Gorin, 303-275-4737, margo.gorin@go.doe.gov
DOE Project Monitor – Bryna Berendzen, 303-275-4946, bryna.berendzen@go.doe.gov

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Executive Summary

The project had a dominant education component. The project involved revising curriculum to educate traditional engineering students in the emerging field of industrial biotechnology. New classes were developed and offered. As a result, the curriculum of the Colorado School of Mines was expanded to include new content. Roughly 100 undergraduates and about 10 graduate students each year benefit from this curricular expansion. The research associated with this project consisted of developing new materials and energy sources from renewable resources. Several significant advances were made, most importantly the heat distortion temperature of polylactide (PLA) was increased through the addition of cellulosic nanowhiskers. The resulting ecobionanocomposites have superior properties which enable the use of renewable resource based plastics in a variety of new applications. Significant amounts of petroleum are thereby saved and considerable environmental benefits also result. The original project objectives had to be modified as a result of DOE funding cuts, the Biomass Program did not receive adequate funding to fully fund its selected projects.

Nonetheless, effectiveness and economic feasibility of the project proved excellent. The educational activities are continuing in a sustainable fashion, now being supported by tuition revenues and the normal budgeting of the University. PI Dorgan taught one of the newly developed classes in the Fall 2006, after the close of the DOE grant, and will do so again repeatedly into the future. Now established, the curriculum in biobased products and energy will grow and evolve through regular teaching and revisions. On the research side, the new plastic materials appear economically feasible and a new collaboration between the PI's group and Sealed Air, a major food-packaging manufacturer, has been established to bring the new green plastics to market.

Public benefits of the project are noteworthy in many respects. These include the development of a better educated workforce and citizenry capable of providing technological innovation as a means of growing the economy and providing jobs. In particular, the educational components addressing the production of bioethanol, biodiesel, and bioplastics provide graduates that can assist American industries in including greater renewable content in feedstocks for materials and fuels. Finally, the collaboration fostered by this grant led to the drafting of a new book entitled, Bioengineering for Sustainability: Materials and Fuels for the 21st Century. This text will be widely available to the public interested in learning more about these important areas of technology.

Comparison of Accomplishments with Goals:

Original Project Objectives:

1. To educate chemists, chemical engineers and materials scientists in the fields of genetic engineering, microbiology, biochemical engineering, and biobased materials by offering a selection of classes designed to broaden their traditional expertise.
2. To educate environmental scientists and microbiologists in the fields of materials science, polymeric materials, and industrial transformations by offering a selection of classes designed to broaden their traditional expertise.
3. To provide outreach services for industry that foster lifelong learning and professional development through offering short classes and web based distance learning services.

Status:

The educational development work (new classes and materials development) was completed. The Colorado School of Mines has expanded its curriculum into the realm of biological processes and products through several mechanisms, including the hiring of faculty biologists and microbiologists, the establishment of centers for biomechanical and biomaterials engineering, and the promotion of an undergraduate minor in the Life Sciences. The goal of this project is to use these and other available avenues to prepare graduate students in Chemical Engineering, Materials Science, and Environmental Science and Engineering for careers in the Biobased Products Industry.

At the Colorado School of Mines, each Ph.D. student is required to complete a 12-credit minor in an outside discipline. A primary goal of the present project was to structure a Biobased Products graduate minor by developing new biomaterials and biotechnology classes to complement existing courses in engineering, materials science, biochemistry, and microbiology. A second primary goal of the project is to incorporate training in biotechnology into the Environmental Science and Engineering graduate curriculum through development of new courses, and a third primary goal is to complement these curriculum development efforts with the establishment and expansion of graduate research projects in the Biobased Products field. The first goal was completed, the needed courses were proposed and the minor program was approved by a vote of the campus Graduate Affairs Committee. Similarly, the secondary goal was successfully met, the new classes developed (discussed below) were developed and offered to roughly 30 students in each case. All of these students have graduated on time for their undergraduate degrees. Unfortunately, because a substantial amount of the originally promised funding for the project was rescinded by the DOE, the graduate level student support was unavailable to fulfill the third objective. Graduate students were supported under other grants and contract from other agencies, most notably, the Environmental Protection Agency.

The courses necessary for the Biobased Products Minor were developed and introduced as an official Graduate Minor occurred in 2002-2003. The minor requires 18 credits and 9 new credit hours have been developed under the grant including:

- ESGN 586: Microbiology of Engineered Environmental Systems
- ESGN 596: Molecular Environmental Biotechnology
- CHEN 426 Biochemical Engineering

A recent development under the auspices of the grant is that the two PIs have co-developed a draft of a textbook entitled, Bioengineering for Sustainability: Materials and Fuels for the 21st Century. The support provided under this grant is directly responsible for the ability of the researchers to collaborate and produce this document.

New class web pages have been developed for the above mentioned classes. These web pages and the accompanying electronic media are now available. These are hosted in the proprietary Blackboard system maintained by the Colorado School of Mines.

In summary, the objectives for the project were met or exceeded. New educational infrastructure was created and is now supported in a sustainable manner. In addition, innovative and important research objectives were met that are allowing the displacement of petroleum-based plastics with renewable resource based ones.

Project Activities:

During the 2001-2002 academic year, the following classes were developed and delivered, with the exception of CHEN 426 which was delivered during the Spring of 2003 semester. The delivered courses were met with great student enthusiasm, obtained high enrollments (~10 per course) for this small university, and have become permanent parts of the CSM curriculum:

- **ESGN 586:** Microbiology of Engineered Environmental Systems. Graduate-level course covering the microbiology of bioremediation, biodegradation, biotransformations, and biological waste treatment, with the theme that microbial processes are becoming increasingly valuable and commercially viable biological products.
- **ESGN 596:** Molecular Environmental Biotechnology. Graduate-level course covering the mechanisms and applications of genetic engineering, including case studies of production of bio-based products and processes such as biodegradable polymer production, biopesticide synthesis, biofuel generation, and biosyntheses of enzymatic detergents, surfactants, biological dyes, and vitamins.
- **CHEN 498:** Introduction to Biochemical Engineering Senior level or first year graduate student class covering the basics of industrial biotechnology from a chemical engineering perspective. Basics of biochemistry and molecular biology, bioreactor design and operation, bioseparations.

Track Development: During the 2001-2002 academic year, the Environmental Science and Engineering Division established a graduate coursework track in Environmental Biotechnology that directly prepares M.S. students for careers in the engineering of biological processes for both process and product-based applications. Track requirements include:

- CHGN 498: Introductory Biochemistry
- ESGN 586: Microbiology of Engineered Environmental Systems
- ESGN 596: Molecular Environmental Biotechnology

Biobased Minor Development: The courses necessary for the Biobased Products Minor are now developed, and introduction of the program as an official Graduate Minor is planned for 2002-2003. The minor requires 12 units from the following courses:

- ESGN 586: Microbiology of Engineered Environmental Systems
- ESGN 596: Molecular Environmental Biotechnology
- CHEN 498 Biochemical Engineering

Research Development: Graduate students and postdocs have been partially supported by funds from the grant, as listed below:

- Scott Plummer (advisor: Ahmann) – Improvement of the iron hydrogenase enzyme in the green alga Chlamydomonas reinhardtii for oxygen-tolerant production of H2.
- Peggy Churchill (advisor: Ahmann) – Isolation and characterization of algal mutants for improved H2 production.
- Lihong Bao (advisor Dorgan) – Permeation properties of BioPlastics and blends thereof

During the 2003-2004 academic year the focus turned to graduate student training and research activities due to the fact that the course development educational objectives had been met and the budget from DOE had been cut (year three funding was reduced from roughly $130,000 to $25,000). A new Ph.D. student, Ms. Birgit Braun, was partially supported under the program. She focused on the synthesis of novel supramolecular nanocomposites containing PLA (polylactide, a corn based plastic). The other constituents of the novel plastics are also derived directly from plants. In particular, we used cellulosics from woody plants and starches from agricultural crops. The creation of PLA-graft-cellulose supramolecular structures holds the promise of addressing one of the key obstacles of greater utilization of plant based materials. Namely, PLA suffers from a low heat distortion temperature as a result of the fact that its glass transition temperature is about 58 C. The supramolecular nanostructures developed using partial support from this project have higher heat distortion temperatures. The background and development of these materials is discussed next.

Petroleum is finite in supply and as world economies continue to develop it will become both more rare and more expensive.(*1*) As a result, less desirable crude oils containing heavy metals such as mercury and contaminants like sulfur are being processed. The resulting extensive pollution along with concerns over climate change due to carbon dioxide emissions make it highly desirable to find alternative sources for fuels and materials. Many communities are also choking in their own solid wastes – much of which consists of plastics: - plastic water bottles in California are filling up available dumping space and when released into the ocean cause a multitude of problems.(*2*) Disposal options are limited in major markets such as California, Japan, and the European Union. As a result of these many profound challenges, sustainability is becoming a leading issue in the plastics industries - “take-back” laws and tipping fees are driving structural changes in plastics use. Manufacturers are now designing for take-back laws to

facilitate rebuilding / upgrading devices or to enable disassembly and materials recovery. These laws and the environmental concerns they are based on demand next-generation technical solutions to maintain the vitality of the plastics industry while simultaneously protecting the environment.

Nanocomposites are a rapidly expanding new plastics technology that offers great promise but for which unknown environmental consequences must be considered. Adding nanosized fillers (minerals, metals, or fibers) to plastics creates a polymer nanocomposite. The worldwide market for such polymer nanocomposites is expected to grow at an average annual growth rate of 18.4 per cent and surpass $211 million by 2008 (by comparison, it reached 24.5 million pounds, or $90.8 million, in 2003).(*4*) Polymer composites are used in many applications and thus sold in billion-pound quantities. As it stands, little is known about the fate and transport and potential toxicity of many of the nanoparticles being deployed in the newly developing field of polymer nanocomposites. If the nanoparticles within the composites do not break down, they will persist in the environment potentially threatening human health. What will happen to the environment, to human and animal health, and to the plastics industries – the fourth largest manufacturing sector of the U.S. economy – if sustainable technologies are not developed and deployed? Degradation of the environment and human health accompanied by additional manufacturing job losses is probable.

The polymer used in this project is polylactide (PLA) made from corn utilizing a combination of advanced fermentation and chemical processing. A comprehensive Life Cycle Inventory (LCI) for PLA using methodology enabling "apples-to-apples" comparisons with petrochemical-based thermoplastics has appeared.(*3*) Among the most notable benefits of PLA are reductions in both fossil fuel use and global warming potential. For example, Figure 2 shows that compared with PET and Nylon, PLA uses 30-50% less fossil resources that results in 50-70% less CO_2 emissions. The carbon in PLA recycles in the earth's carbon cycle, in the same manner as plants. Reduced fossil energy input is needed because energy from the sun provides one-third of the Gross Energy Requirement in PLA; conventional plastics rely solely on oil reserves for their content. Natureworks Inc., the manufacturer of PLA, now uses renewable energy credits to run its manufacturing plant in Blair, Nebraska – simply put, PLA is the most environmentally friendly plastic material ever produced.

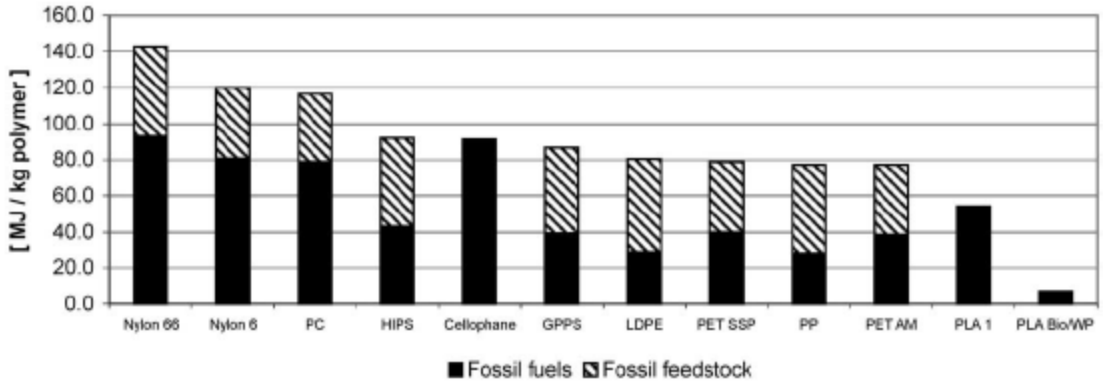

Figure 2. Life cycle analysis results for energy content of various thermoplastic polymers. PLA has the lowest non-renewable energy content (Note: PLA Bio/WP is the projection for the production of PLA using wind power(WP) and agricultural byproducts – WP is now used).

If PLA is so favorable from a sustainability perspective, then why is it not more widely used? One reason is that PLA was only recently commercialized and been made available in large (millions of pounds annually) quantities. Another reason, the one most pertinent to the proposed research, is that the property window of the homopolymer is limited (see below). Accordingly, producing ecobionanocomposites that have better properties than the base PLA in an economical manner was the objective of this Phase I research project.

PLA does have sufficient physical properties for a variety of applications (textile fibers, plastic trays, some film applications) but its use is restricted to low temperatures. That is, the heat distortion temperature (HDT) is limited because PLA has relatively low glass transition temperature (T_g). The T_g of PLA is around 55-60°C, depending on molecular weight and stereochemical composition, leading to an HDT of approximately 70°C. This inability to be used at higher temperatures precludes the use of PLA in many applications such as microwaveable food packaging, plastic cutlery for hot foods, coffee stirrers, foamed cups for hot liquids, and articles such as disposable razors. Another difficulty is that PLA is too permeable to carbon dioxide and water to serve as a beverage bottles – one of the primary components of our nation's solid waste volume. Currently, for PLA to be used as a beverage bottle with a sufficient shelf-life, it must be filled with a mineral that is mined and then chemically treated with undesirable chemical coupling agents. Finally, PLA by itself is too brittle to serve in papercoating (where degradability is very desirable) as it tends to crack when cardboard is folded into items such as juice boxes or milk cartons. Currently, when used in papercoating, the environmentally benign PLA must be combined with plasticizers such as DOA and DOP. There is considerable concern about the estrogen mimicking nature of these plasticizers – enough so that they have been removed from children's toys. Fortunately, nanocomposite technology can address these property shortcomings without the need to resort to environmentally questionable chemical modifications.

Research Work Carried Out

The objective of the graduate student's project was to demonstrate that it is possible to use nanotechnology to increase the HDT of PLA. The technical approach was experimental in nature, relying on established chemical engineering principles.

Task A - Nanowhisker Synthesis and Dispersion

A1. Set reaction conditions – Our procedure was refined to use concentrated hydrochloric acid for 20 minutes at 100° C in an agitated glassware vessel. We found that cotton is the best feedstock (rather than Aspen) because cotton produced the greatest yield of cellulosic whiskers with dimensions in the nanometer range. Also, it was discovered that hydrochloric acid produces whiskers with greater thermal stability than sulfuric acid (see Results).

A2. Develop isolation procedures – literature isolation techniques (i.e., membrane dialysis) are limited so alternative procedures have been developed. Centrifugation was identified as a more industrially practicable process as the scale of production increases and was been adopted. PolyNEW was able to successfully use centrifugation of the products of reaction to isolate the cellulosic nanowhiskers.

A3. Develop combined Reaction-Separation – Process optimization to maximize the yield of cellulosic nanowhiskers is needed. Repeated mechanical agitation combined with centrifugation was investigated as a route towards optimization of nanowhisker yield.

A4. Produce cellulosic nanowhiskers – the production of cellulosic nanowhiskers in sufficient quantities to complete Task B was completed as planned.

The measurable outcome of Task A was the existence of nanowhiskers in 15-20 lb. lots. We are now able to produce such batches.

Task B – Nanocomposite Manufacturing

In this task a small-scale twin-screw mixer was used to pilot the manufacturing process. In twin-screw extrusion there are important processing variables to be considered. To assess these processing variables and related questions, an experimental design (reported in Table 1) identifies the factors and levels.

Based on preliminary experimentation, we have also found that premixing of the lactide with the cellulosic nanowhiskers was highly advantageous. Accordingly, we slightly modified the experimental design to account for this (replacing the static mixer with premixing in the plan).

Table 1. Experimental design for nanocomposite manufacture.

Factor		Levels	
Lactide feed location	Feed Throat		Liquid Injection Port
Nanowhisker feed location	Feed Throat	Side Stuffer	
Polymerization catalysts injection location	Feed Throat		Liquid Injection Port
Transesterification catalysts injection location	Feed Throat		Liquid Injection Port
Nanowhisker loading level	35% by weight	20% by weight	
Reaction Zone Temperature	250 °C	220 °C	
Premixing	Present	Absent	

The measurable outcome of Task B was a series of novel biobased nanocomposite materials that were characterized in Task C.

Task C – Nanocomposite Property Evaluation (Months 3 - 6)

Under this task, the materials produced under Task B were characterized in order to demonstrate their superior nature.

C1. Measure thermo-mechanical properties. Thermal properties were of greatest interest (T_g measured by DSC and the HDT measured by DMTA). Standard protocols for all testing were developed and followed.

- Glass transition (T_g), melting (T_m), and percent crystallinity (%Cryst) were measured by differential scanning calorimetry (DSC).
- Molding test specimens was accomplished using existing compression molds.
- The heat distortion temperature (HDT) of sample was measured using dynamic mechanical thermal analysis (DMTA).
- Testing dogbone samples for mechanical properties including modulus, strength, and strain at break was completed using an Instron test station.

Results Obtained

There is an immediate, large, and open market for a PLA based material with an enhanced HDT is in solid and foamed trays. Projections at this time suggest an annual consumption of 15 to 20 million lbs./year of PLA in this application, assuming the transport and storage temperature limitation can be overcome. For simple low temperature applications such as case ready trays and the like, the HDT issue is one of transportation and storage and the technical target is an HDT>80°C. Moving beyond this to microwaveable tray applications, the HDT would have to be > 100 to 105°C. As shown again in Figure 3, both of these technical objectives have been met using the cellulosic nanocomposite technology developed in Phase I.

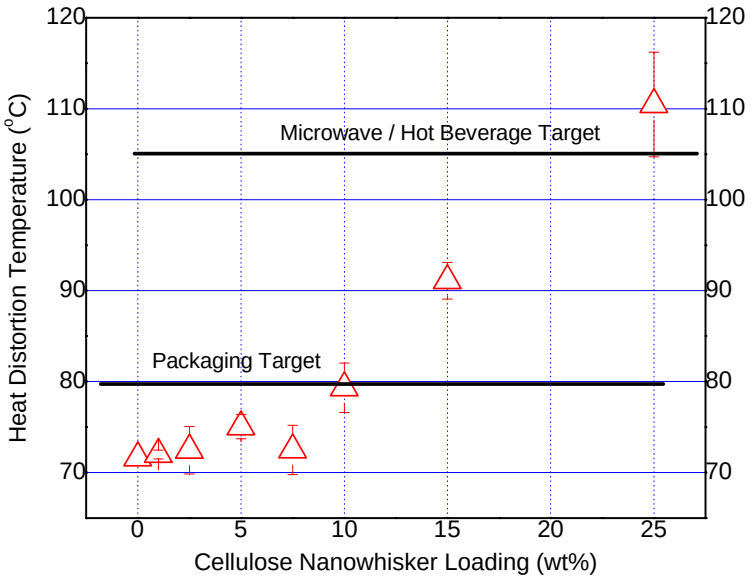

Figure 3. HDT vs. Cellulose loading level. Both secondary and primary targets were met in Phase I allowing the development of a material in Phase II with an annual market of 15 to 20 million pounds per years corresponding to 15 to 20 million dollars in annual revenue.

In addition to meeting the technical targets associated with HDT, the new materials exhibit superior moduli. Moduli data are shown in Figure 8 below.

Methodologies for producing stable nanowhiskers were also developed. Representative micrographs are presented in Figure 6. Thermal stability of the whiskers synthesized using hydrochloric acid were found to be superior to those synthesized using sulfuric acid; these results are highlighted in Figures 4 and 5.

Task A - Nanowhisker Synthesis and Dispersion

Early in our investigations, we changed our cellulose feedstock to cotton linters and acid to hydrochloric acid. We found that hydrochloric acid produced more thermally stable whiskers.

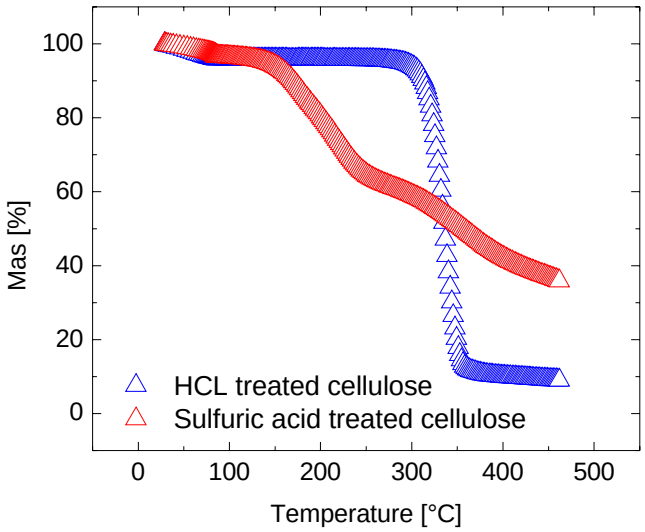

Figure 4. Comparison of the thermal stability of cellulosic nanowhiskers prepared using hydrochloric (HCl) and sulfuric acids. Mass versus temperature is recorded in a thermal gravimetric analyzer (TGA). The HCl produced whiskers have greater thermal stability.

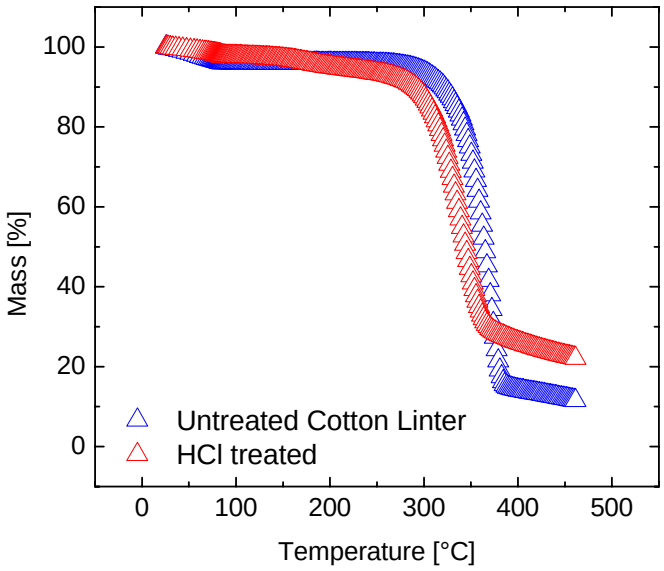

Figure 5. Comparison of HCl nanowhiskers with original biomass source showing only moderate changes in thermal stability.

The laboratory procedure for preparing cellulose nanowhiskers (CNW) is divided into three main steps. The process we developed and followed is described below.

Acid Digestion Step

- Cotton linter was mixed with hydrochloric acid to obtain a concentration of approximately 10% by weight cotton linter and achieve an acid concentration of 2.5 N. This procedure generally follows the method of Battista (*5*)
- The correct acid concentration is achieved by diluting a standard 37% HCl solution (industrially available strength) with water to 2.5 N HCl.
- The dilution water was added first to the cotton linters and blended in an industrial Waring blender to facilitate breakup of the linters. The concentrated acid was then added to the linter slurry.
- The acidic linter slurry was transferred to the glass reactor vessel and heated to 100 °C. The slurry was vigorously mixed for 20 minutes. During the mixing time, the linter pieces gradually disintegrated.
- After 20 minutes of mixing, the heating media was removed and the linter suspension was cooled to room temperature.

Acid Separation and Cellulose Washing/Neutralization

- To separate the cellulose from the acid solution the suspension was centrifuged at 10,000 rpm for 3 minutes, and the clear supernatant decanted. Fresh water equal in volume to the supernatant that was decanted, was then added back to the cellulose cake to wash and neutralize the material. The step was repeated multiple times to investigate the progression of the pH of wash solution. It took 5 repeated washing cycles to reach a pH of 5 (tested using pH indicator paper) The pH development was as follows:

Wash	**pH**
1st Wash	0
2nd Wash	2
3rd Wash	3
4th Wash	4
5th Wash	5

- In an industrial process, the cellulose would be washed once and the acidic washwater would be neutralized and recycled as necessary.
- At pH = 5, the supernatant remains turbid after centrifugation; this can be used as indication, that the suspension is neutralized.
- After the 5th wash, the supernatant was collected and analyzed for solids content using the TGA. Solids content was found to be0.0015g/ml.

Drying

- At this point, to use the CNW in our composite, the cellulose cake was dried in a freeze-dryer for subsequent dispersion directly into lactide.

In order to examine the structure and size of the whiskers produced, a portion of the cellulose cake was also dispersed into water using an industrial Waring blender. A drop of the CNW whiskers in suspension was dried onto a glass slide and examined under the scanning electron microscope (SEM). Figure 6 shows an image of CNWs produced, with whiskers having diameters in the range of 40-55nm and lengths from 300 to 500 nm.

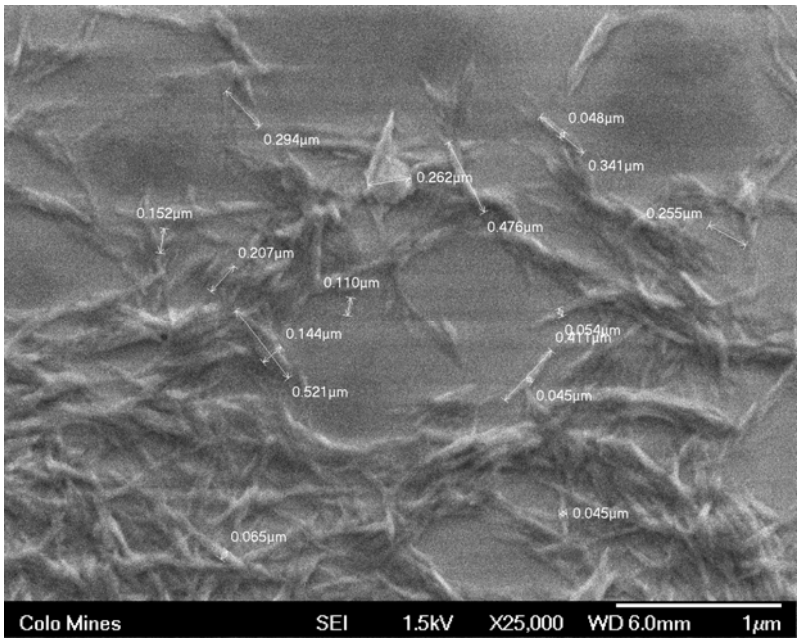

Figure 6. SEM Image of Cellulose Nanowhiskers

Task B – Nanocomposite Manufacturing

Following the experimental design, the large collection of materials was produced. In addition to materials synthesis, feed material preparation procedures and CNW pre-mixing operations were developed. It was found that pre-mixing the CNW directly with the lactide was the best methodology for introducing the feed materials to the extruder. Our final optimized methodology for feed material preparation, premixing and polymerization are described below.

Feed Material Preparation

- Stock solutions of catalyst (stannous octoate) and stabilizer (tris(nonylphenyl)phosphate (TNPP)) were prepared in dry toluene. Stannous octoate and TNPP were obtained from Sigma Aldrich. Stannous octoate was distilled before use; TNPP was used as received.
- CNW and lactide were dried under direct vacuum (mtorr range) at room temperature for 24 to 48 hours. Lactide was obtained from Natureworks and was used without further purification.

Premixing Operation

- Dried lactide was measured out into a covered vessel and blanketed with Argon.
- Dried CNWs were measured out to get a 25% wt cellulose mixture, blanketed with Argon and covered.
- The mixer assembly was pre-heated to 104 °C.
- The lactide was melted in a covered vessel at approximately 110°C until it was completely melted.
- 1 wt% TNPP (compared to lactide) was added to the melted lactide.
- The melted lactide was then added to the pre-heated mixer, the mixer was covered and the mixing commenced.
- The CNWs were added to the lactide while the mixer was running.

- The suspension was mixed for 20 minutes on HI speed, while maintaining temperature below 115 °C.
- At the end of the mixing time, the suspension was carefully poured/drained into a dried pan, blanket with argon, and covered until cooled.
- When the fiber/lactide mixture was cooled, it was crushed. The crushed material was dried under vacuum at room temperature for 24 hours. It is now ready to add to the extruder for polymerization

Polymerization

- The crushed dried CNW/lactide mixture was added at a constant rate to the reactor
- Catalyst in the ratio of 2500 moles lactide to moles stannous octoate was added to the extruder to catalyze the polymerization reaction.
- The polymerization was carried out at a reaction temperature of 180°C with a residence time of 30 minutes.
- Cellulose loading levels between 1% and 25 % were evaluated.

Task C – Nanocomposite Property Evaluation

C1. Measure thermo-mechanical properties

Differential scanning calorimetry (DSC) measurements were conducted on all samples; glass transition (T_g), melting (T_m), and percent crystallinity (%Cryst) were determined. A Perkin-Elmer DSC-7 was used to perform these measurements. Tested materials were first devolatilized in a 120 °C vacuum oven for 48 hours. Because of this treatment, the first heating scan was used to determine the T_g's and %Cryst. A representative scan is presented in Figure 7.

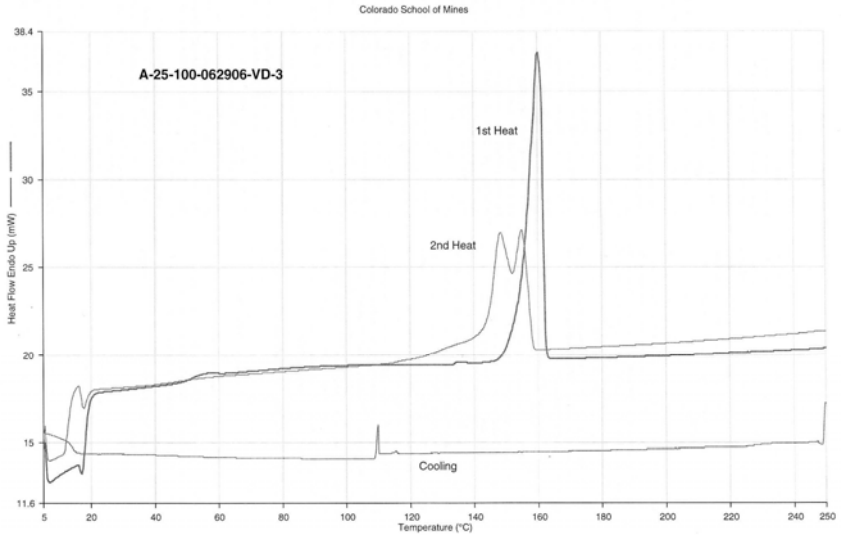

Figure 7. Representative DSC trace showing glass transition and melting temperatures.

Measured T_gs were used as a screening test during polymer production to determine the most promising materials for mechanical testing.

Molding of test specimens was accomplished using existing compression molds and a Carver hot press. The molding procedure approximately followed the method of Teramoto et al. (*6*) The

specimens were granulated, dried, and then molded by pressing between hot plates; these samples were subsequently allowed to physically age for 12 hours at room temperature prior to testing. The heat distortion temperature (HDT) of samples was measured using dynamic mechanical thermal analysis (DMTA) using torsional rectangular fixtures on an ARES-LS Rheometer (TA Instruments). ASTM method D-648 is the standard technique for determining HDT of polymers. (*7*) This test subjects a polymer bar of dimensions 127×13×3 mm to an edgewise load of 1.82 MPa. The heat distortion temperature is defined as the temperature at which a sample bar deflects 0.25 mm. Takemori has correlated polymeric modulus-temperature behavior under these same test conditions and found the equivalent HDT to be the temperature where Young's modulus reaches a value of 0.75 GPa. (*8*) Accordingly, this equivalent technique was adopted to determine the HDT using the ARES rheometer.

The ARES-LS reports values for G' (storage modulus) and G" (loss modulus).

$$G^* = G' + iG''$$
$$G = \left|G^*\right| = \sqrt{G'^2 + G''^2} \quad (1)$$

and Young's modulus is calculated from these values as follows:

$$E = 2(1+v)G \quad (2)$$

The calculation uses a value of v = 0.33 for PLA, which is characteristic of glassy polymers. The average HDT versus cellulose loading level is shown in Figure 3. This figure shows that the technical target of producing a material with an HDT of 105 °C was met! A complete summary of data obtained by DMTA, including modulus, T_g and HDT is provided in Appendix C.

Testing dogbone samples for mechanical properties including modulus, strength, and strain at break was completed using an Instron test station. The results of the tensile testing is provided in Figure 8. A typical tradeoff of increasing modulus and decreasing extension to break was observed; it is felt that the improved moduli add additional value to the composite materials.

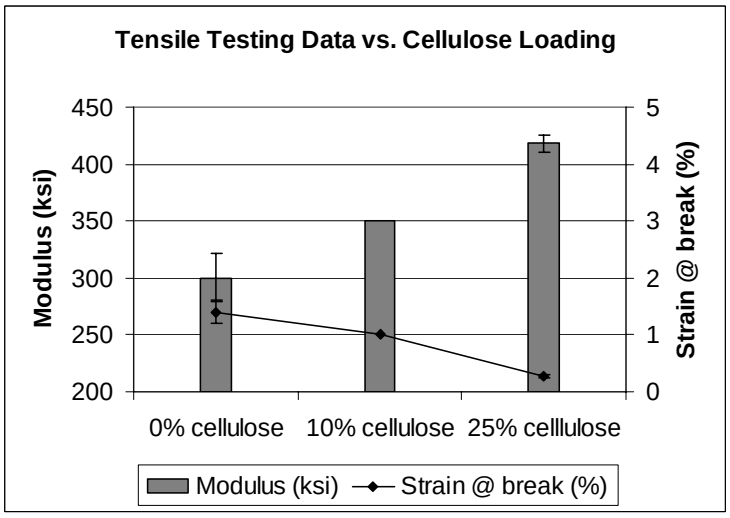

Figure 8. Modulus and strain at break for sustainable nanocomposites.

Professor Dorgan also organized the annual meeting of the Bioenvironmental Polymer Society (BEPS) which was held on August 10th-13th in Denver. Professor Dorgan served as the Vice President 2004 and as President of BEPS in 2005. This is considered an educational outreach activity under the grant as it provided public information about the ability to use renewable, biobased materials in place on depleting petroleum based materials.

During the 2004-2005 academic year our research continued and publications resulted. In addition, work was completed on the text, Bioengineering for Sustainability: Materials and Fuels for the 21st Century. Our research work under the grant was featured in Chemical and Engineering News, the biweekly publication of the American Chemical Society. In an article entitled, Green Polymers field is Blossoming (Michael Freemantle in Chemical and Engineering News (October 2nd, 2005 issue) Our research advances in making improved forms of biobased plastics were cited as significant developments. This is primarily due to the fact that we are exploiting nanotechnology to improve the thermophysical properties of biobased plastics.

Our work has proven that reactively prepared nanocomposites of PLA with microcrystalline cellulose do in fact show enhanced heat distortion temperatures. Present formulations have HDTs in excess of 100 C thereby allowing the use of biobased PLA in a variety of hot food and hot drink applications.

Products Developed:

A. Publications

1. Novel Reactively Compatibilized Microcomposites, John R. Dorgan and Birgit Braun, Polymer Preprints 46(1), 287, (2005)
2. Ecobionanocomposites: A New Class of Green Materials, John R. Dorgan and Birgit Braun, Polymeric Materials: Science and Engineering Preprints 93, 954, (2005)
3. Reactively Compatibilized Cellulosic Polylactide Microcomposites, Birgit Braun , John R. Dorgan, Daniel M. Knauss, Journal of Polymers and the Environment 14(1), 49-58, (2006).

B. Web sites

http://www.mines.edu/Academic/chemeng/faculty/jdorgan/

http://blackboard.mines.edu/webapps/portal/frameset.jsp?tab=courses&url=/bin/common/course.pl?course_id=_2647_1

http://blackboard.mines.edu/webapps/portal/frameset.jsp?tab=courses&url=/bin/common/course.pl?course_id=_2274_1

C. Collaborations Fostered

A wide variety of collaborations were fostered, at least in part, due to the present grant. These include the direrct collaboration between the PI and co-PI that led to the draft manuscript of the book, Bioengineering for Sustainability: Materials and Fuels for the 21st Century. In addition, ties

between CSM and NREL were enhanced; presently there is a Memorandum of Understanding (MOU) in place to facilitate research between the CSM group and NREL by allowing shared use of laboratory facilities. CSM graduate students can be badged for security clearance and facile access to NREL laboratories and facilities. Finally, having publishable research results in the PLA plastics area has led to additional interactions with USDA researchers (largely through the BEPS meetings) and with several industrial research groups including Ford Motors, Kodak, and Sealed Air. Additionally, collaboration with other academic groups, notably at Clemson University, have also been enhanced.

D. Technologies

The development of PLA bioplastics with enhanced properties represents a significant advance in the state-of-the-art for biobased materials. This has led to additional funding and the collaboration with Sealed-Air is working towards commercialization of these new materials for use in food packaging applications

E. Patents:

A patent entitled, HIGH MODULUS POLYMER COMPOSITES AND METHODS OF MAKING THE SAME was filed with the USPTO.

F. References:

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3. E. T. H. Vink, K. R. Ra´ bago, D. A. Glassner, P. R. Gruber, *Polymer Degradation and Stability* **80**, 403 (2003).
4. L. A. Utraki, K. C. Cole, *Polym. Eng. Sci.*, 1799 (2002).
5. O. A. Battista, P. A. Smith., *Ind. Eng. Chem.* **54**, 20 (1962.).
6. Teramoto, Y., Nishio Y., *Polymer* **44**, 2701 (2003).
7. ASTM, 8.01-8.03, D 648, American Society for Testing and Materials (2004).
8. M. T. Takemori, *Polym. Eng. Sci.* **19**, 1104 (1979).